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A sample of high-grade commercial "iso-octane" was purified further by subjecting it to a number of fractionations by equilibrium melting in a centrifuge.[4] As a result of these fractionations four different fractions with freezing points ranging from −107.7° to −107.4° C. were obtained. The time-temperature cooling curve of the purest fraction of "iso-octane" was determined, and is shown in Figure 1.

From the value, −107.41° C., found for the freezing point of pure iso-octane and from Parks and Huffman's value [5] (18.9 cal./g) for the heat of fusion, the purity of the iso-octane may be calculated from the laws of ideal solutions and is expressed by the equation: $P=3.86_2t_F+514.8$ in which t_F is the initial freezing point of the sample in ° C., and P is the purity in mole per cent.

Temperatures were determined by means of a platinum-resistance thermometer calibrated at this bureau in accordance with the International Temperature Scale [6] as adopted in 1927.

WASHINGTON, May 4, 1932.

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[4] For method see M. M. Hicks-Bruun and J. H. Bruun, B. S. Jour. Research, vol. 8, p. 527, 1932.
[5] See footnote 3, p. 269.
[6] B. S. Jour. Research, vol. 1, p. 635, 1928.

A TWIN-BOMB METHOD FOR THE ACCURATE DETERMINATION OF PRESSURE-VOLUME-TEMPERATURE DATA AND A SIMPLE METHOD FOR THE ACCURATE MEASUREMENT OF HIGH PRESSURES

By Edward W. Washburn

ABSTRACT

By filling one bomb, A, with the system under investigation and a twin bomb, B, with a reference substance and then adjusting the two pressures to exact equality (at a given temperature) with the aid of a pressure equalizer, the ratio of $\frac{PV_0}{T}$ per gram for the two systems can be accurately determined by weighing the two bombs. No pressure measurements are involved. If now the volume of bomb B is known, the value of $\frac{PV_0}{T}$ for the system under investigation can be computed to the accuracy with which $\frac{PV_0}{T}$ is known for the reference substance.

Furthermore, if a gas-filled bomb of volume V at a known temperature, T, is brought into pressure equilibrium with any system at the pressure P and the mass of the contained gas determined, the value of P can be computed with the accuracy to which $\frac{PV_0}{T}$ is known for the gas employed. In this way an ordinary balance and weights can be utilized as a laboratory tool for the accurate measurement of high pressures.

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I. INTRODUCTION

For practical purposes the task of accumulating accurate physical data concerning chemical substances and systems may be roughly divided into two categories. To the first category belong those pri-

mary measurements in which the measuring instruments employed are more or less directly standardized in terms of the fundamental units of science, for example in cgs (*e* or *m*) °K. units.[1] Such measurements may be called primary or "absolute" measurements to distinguish them from the second category, which may be designated as secondary or relative measurements.

This category comprises measurements in which the apparatus and instruments employed are in part at least, standardized with the aid of a substance or material for which accurate values are available from primary measurements carried out as outlined above or which is selected by convention as the reference substance.

Measurements in this class are fundamentally relative measurements, but they can be converted to absolute values through the standardizing material employed, and if the accuracy of the relative measurements is sufficient, the absolute values obtained in this way should be as reliable as are the primary data for the standardizing substance. Examples of measurements belonging to the second category are the determination of the viscosity of a liquid with a viscosimeter standardized with water and the determination of the heat of combustion of an organic substance with a bomb calorimetric equipment standardized with benzoic acid.

In some cases the relative measurements are so much more precise than any primary measurements that a conventional value is sometimes adopted for the standardizing substance. This conventional value may be purely arbitrary, as in the atomic weight table, or it may be the best at-the-time available absolute value with zeros assumed in all places following the last known figure, as in the measurement of current in so-called "international amperes" by means of a silver coulometer.

The relative method frequently has the advantage of greater rapidity in the measurements combined with simplicity and relative inexpensiveness in the equipment required, these advantages being sometimes combined with a higher degree of accuracy than that obtainable in the absolute measurements.

So far as the writer is aware, no attempt has been made to determine directly and accurately the ratio of PV/T for two gases at high pressures.[2] The purpose of this paper is to outline a simple method for doing this and to show that this method may be extended to the determination of pressure-volume-temperature data for any system.

II. EQUIPMENT

The equipment to be employed consists of:

1. A pair of twin bombs as nearly identical as possible in all respects.
2. Inexpensive Bourdon gages.
3. A good thermometer.
4. A well-stirred constant-temperature bath, or baths, variable over the temperature range desired.
5. A good balance and set of weights.
6. Means for obtaining the gases under the desired pressures.

No accurate pressure measuring equipment is required.

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[1] Centimeter, gram, second (electrostatic or electromagnetic), °K.

[2] For very low pressures, below 1 atmosphere, an interesting and accurate relative method has been described by Addingley and Whytlaw-Gray, Trans. Faraday Soc., vol. 24, p. 378, 1928.

III. EXPERIMENTAL PROCEDURE

The investigator first selects, on the basis of available data, a reference gas (or gases) for which satisfactory P–V–T values are available over the pressure and temperature ranges within which he proposes to make his measurements. A typical experiment is carried out as follows: With the aid of an ordinary Bourdon gage one of the bombs is filled at about $t°$ C. with the reference gas, R, at a pressure slightly above that desired for the experiment. The second bomb is filled in the same way with the gas, E, under investigation. Both bombs are placed side by side in the constant-temperature bath regulated to the desired temperature, $t°$ C., and each one is then joined through capillary tubing (and a guard bomb if desired) to a pressure equalizer, for example, a large cylinder containing air (or other suitable fluid) at a pressure slightly below the pressure in the two bombs, and provided with a Bourdon gauge.

The valves of the two bombs are now opened simultaneously and when temperature equilibrium has been attained, the valves are closed, the capillary tubing is disconnected, and the bombs are removed from the bath, dried, and the difference in mass accurately determined. One of the bombs is then evacuated and the difference in mass again determined in the same way, or either of the two may be weighed against a closed dummy bomb of known mass. The ratio of $\frac{PV}{T}$ for unit masses of the two gases can now be calculated, as explained in section VII below.

IV. CONSTRUCTION OF THE TWIN BOMBS

The material used for constructing the bombs will be determined by the nature of the gas to be investigated and the pressure and temperature ranges to be covered.[3] The material selected and the wall thickness adopted should be such that the strain on the bomb will be well within the elastic limit. The thoroughly annealed bomb before calibration is first put through a number of cycles of compression and decompression (filling and emptying) with compressed gas, for the maximum pressure for which it is to be utilized at each temperature. It is now ready for calibration.

The calibration consists in determining the volume of one of the bombs and in determining, or reducing to a negligible amount, two small quantities both of which would be zero, if the bombs were identical twins. These two quantities are the difference in the masses and the difference in the volumes of the two bombs.

V. DETERMINATION AND EQUALIZATION OF THE VOLUMES OF THE TWIN BOMBS

With the aid of the constant-temperature bath and pressure equalizer described above, both bombs are filled with the same gas at the same moderate pressure (preferably a dense gas, such as CO_2,

[3] A discussion of materials suitable for containers for various conditions of temperature, pressure, and corrosive influences has been given by F. G. Keyes (Ind. Eng. Chem., vol. 23, p. 1378, 1931).

purity not essential) or with the same liquid, and the difference, $m_1 - m_2$, in the masses of the fluid, together with the mass, m_1, in one of the bombs is determined as in a regular experiment. The difference in the two volumes is given by the relation

$$\Delta V = V_1 - V_2 = \frac{(m_1 - m_2) V_1}{m_1} \tag{1}$$

To the larger of the two bombs there is now added, in the form of fine shot or wire for example, the right amount of a material, having negligible vapor pressure and negligible (or known) compressibility, to adjust the volumes to exact equality. There is some advantage in using for this purpose the material of the bomb itself.

After this adjustment has been made the now-much-smaller ΔV may be determined as a function of p and T over the proposed experimental range. If the construction and adjustment of the two bombs have been carefully carried out, this value of ΔV should be negligible.

The bombs having been adjusted to equality of volume, the volume of one of them is now determined as a function of pressure and temperature. For atmospheric pressure (zero pressure difference) this value will be known from the above determinations, if the density of the fluid used is known. The temperature coefficient can be calculated from the coefficient of thermal expansion of the bomb or the volume may be determined by calibration at different temperatures.

The small pressure coefficient can, for many purposes, be determined with the necessary accuracy by immersing all but the stem of the bomb in the liquid of a volumeter and reading the increases in volume of this liquid as successively increasing pressures are applied to the bomb. It may also be calculated from the elastic properties of the material composing the bomb. Formulas for this purpose have been given by F. G. Keyes.[4]

For the most accurate work, especially for extreme conditions of temperature and pressure, it may be necessary to check the volume calibration from time to time because of possible hysteresis effects.

VI. EQUALIZATION OF THE MASSES OF THE TWIN BOMBS

The evacuated bombs are now suspended from the arms of a sensitive balance and the masses are adjusted to equality. At the same time a closed dummy bomb can also be provided, if desired, and similarly adjusted to the same mass. This dummy may be employed as a counterpoise for determining the total mass of the gas in one of the bombs, as indicated in the procedure outlined in Section III above.

VII. COMPUTATION OF THE $\frac{PV_0}{T}$ RATIO

From the data obtained by the procedure described in Section III the value of $\pi_E = \frac{PV_0}{T}$ for unit mass of any gas at the pressure and temperature of the experiment is obtained from the relation

$$\frac{\pi_E}{\pi_R} = (1 - \Delta V/V_R)\ (1 + \Delta m/m_E) \tag{2}$$

[4] See footnote 3, p. 273.

in which π_R is the value of $\frac{PV_0}{T}$ for the reference gas at the pressure and temperature of the experiment; V_R is the volume of the reference gas; $\Delta V, = V_R - V_E$, is the difference in the volumes of the two gases; m_E is the mass of the gas under investigation; and $\Delta m, = m_R - m_E$, is the difference in the masses of the two gases. After completing the experiment as described above, it may be repeated by interchanging the gases in the two bombs and ΔV may be eliminated from the two equations thus obtained.

Judging from the precision which should apparently be attainable in the measured quantities, the relative values obtained in this way should be more accurate than many of the absolute values at present available.

VIII. COMPUTATION OF $\frac{PV_0}{T}$ FOR THE REFERENCE GAS

In order to convert into absolute values the relative values obtained by the above procedure, it is necessary to compute the value of π for the reference gas. If the data for this gas have been put into mathematical form by evaluating the parameters of an equation of state in which π is given as a function of V and T, then the value of π is readily calculable since both V and T are known with the necessary accuracy. If only tabulated values of $\frac{PV_0}{T}$ are available for various temperatures and for a series of pressures, then the experimental temperatures employed should include those available for the reference gas and the value of π_R can be obtained by graphing values of $\frac{PV_0}{T}$ against $\frac{T}{V_0}$ in the experimental region and interpolating π_R for the known value T/V_0. At the same time the value of P is obtained to the degree of accuracy corresponding to that of the $\frac{PV_0}{T}$ data of the reference gas.

IX. ACCURACY REQUIRED IN THE MASS DETERMINATIONS

For any specific case the accuracy required in the weighings for any given desired accuracy in π_E/π_R can be judged by inspection of equation (2).

In general, it may be said that an accuracy of 0.01 per cent in π_E/π_R should be practically always attainable, or stated in another way, the masses of the bombs will never need to be so great as to render difficult the attainment of the required accuracy in the weighing operations, and this accuracy will be obtainable with a comparatively inexpensive balance, except possibly in the cases of hydrogen and helium where a balance of high sensitivity might be needed. (See further, Sec. XIV below.)

X. ACCURACY REQUIRED IN THE VOLUME DETERMINATIONS

If the volumes of the two bombs are adjusted to substantial equality, a large percentage error is obviously allowable in both ΔV and V in determining the value of π_E/π_R. For interpolating the absolute value of π_R, V_R must be known with an accuracy which varies with the slope of the $\pi - \frac{T}{V_0}$ curve for the reference gas in the experimental region. Thus, for a considerable region on both sides of the Boyle pressure,[5] large errors in V_R will have but little effect upon the result. In any case V_R can be determined with the required accuracy.

XI. SELECTION OF THE REFERENCE GAS

Since relative values of $\frac{PV_0}{T}$ can be determined with a high degree of accuracy and with comparatively simple equipment, absolute values should be available for one or for a few gases selected on the basis of their advantages as reference gases and these values should be known as accurately as possible and should cover a wide range of temperatures and pressures.

Among the gases which might be selected as suitable reference gases, air has the disadvantages of its oxidizing action at high temperatures and its lack of constancy in composition.[6] In spite of these disadvantages, however, dry, CO_2-free air is likely to be the favored reference gas for measurements of moderate accuracy, say ± 0.1 per cent, because of its ready accessibility. For this reason reliable P–V–T data should be available for air (of known normal density) over wide ranges of temperature and pressure. Furthermore, if the investigator who proposes to use air as a reference gas determines the normal density of the sample of air employed, air would probably be suitable as a reference gas even for measurements of the highest accuracy.

A review of the various other possibilities leads to the conclusion that "atmospheric nitrogen",[6] methane, and carbon dioxide would be suitable as additional reference gases. These gases can be prepared in a high state of purity at reasonable cost. Carbon dioxide could be used for investigations confined to temperatures above, say, 40° C., while methane could be used for temperatures between, say, 200° and −80° C. "Atmospheric nitrogen" could be used at any temperature above, say, −140° C.

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[5] That pressure at which for a given temperature the PV product is a minimum.

[6] See the extensive data on this question recently obtained by Moles (Gazz. Chim. Ital., vol. 56, p. 915, 1926). This investigator also found that after chemical removal of the oxygen from air, the residue, "atmospheric nitrogen," showed a much more nearly constant density, the maximum variation found being only 1 in 10,000. Apparently, therefore, "atmospheric nitrogen" would be an excellent reference gas for wide ranges of temperature and pressure.

XII. ADAPTATION OF THE METHOD TO LIQUIDS AND SOLIDS AND TO POLYPHASE SYSTEMS

It is obvious from the foregoing discussion that the method described in this paper might also be applied to the determination of P–V–T relations in many systems composed of or containing one or more solid or liquid phases. For this purpose a retaining or immersing liquid may be needed or preferred in the bomb containing the system under investigation and in that case the gas-filled bomb functions purely as a pressure gage.

XIII. THE USE OF A GAS-FILLED BOMB AS A PRESSURE GAGE

If a gas-filled bomb of known volume and temperature is brought into pressure equilibrium with a system at the pressure P, with the aid either of a pressure equalizer such as that described above or with the aid of a nul-point differential gage,[7] and the mass of gas in the bomb determined, then its pressure can be calculated as indicated above and the value thus obtained will be as accurate as are the available PV_0/T data for the gas employed. In this way a balance and weights can be utilized as a laboratory tool for the accurate measurement of high pressures.

The accuracy required in V and T will be determined by the accuracy wanted in P or by the accuracy possessed by $\frac{PV_0}{T}$, whichever happens to be the determining quantity.

The method might also find some application for calibrating an electrical or mechanical pressure gage, in case a dead-weight pressure gage is not available.

XIV. DETERMINATION OF THE MASS OF THE GAS AFTER REMOVAL FROM THE BOMB

The range of pressure over which a given pair of twin bombs can be employed is limited on the high pressure side by the elastic limit of the material of which the bomb is composed and on the low-pressure side by the mass of contained gas which can be determined with the required accuracy by weighing the bomb. If, therefore, a given gas is to be investigated over a very wide range of pressures, a set of bombs would be required. For many gases this necessity can be avoided and a single pair of heavy-walled bombs can be employed in all parts of the pressure range by arranging to remove the gas from the bomb for the purpose of weighing it. Thus CO_2 could be weighed after condensation or after absorption in ascarite (NaOH-asbestos mixture), H_2O and certain alcohols after absorption in Dehydrite ($Mg(ClO_4)_2 \cdot 3H_2O$), a combustible gas after passage through a combustion furnace followed by absorption of CO_2 and/orH_2O as above, etc. These methods are somewhat more time-consuming than direct weighing, but a high degree of accuracy is obtainable and certain other obvious advantages are secured.

[7] For example, the sensitive differential gage described by Osborn, Stimson, and Fiock, B. S. Jour. Research, vol. 5, p. 430, 1930. The differential gage is required whenever direct contact between the system and the fluid of a pressure equalizer is undesirable.

XV. CONCLUSION

The method outlined above will probably find its chief application in chemical laboratories and industrial laboratories which do not have available accurate dead-weight pressure gages, but in which the need occasionally arises of obtaining *P-V-T-* data for gases and vapors and their mixtures. The recent publication of several papers giving rather rough data of this character obtained with Bourdon gages illustrates a growing need for reliable *P-V-T* data for a considerable number of gases and gas mixtures for which no information is at present available. It is hoped that the method described in this paper may be found useful to the occasional investigator who finds it necessary to determine such data for himself.

WASHINGTON, December 28, 1931.

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